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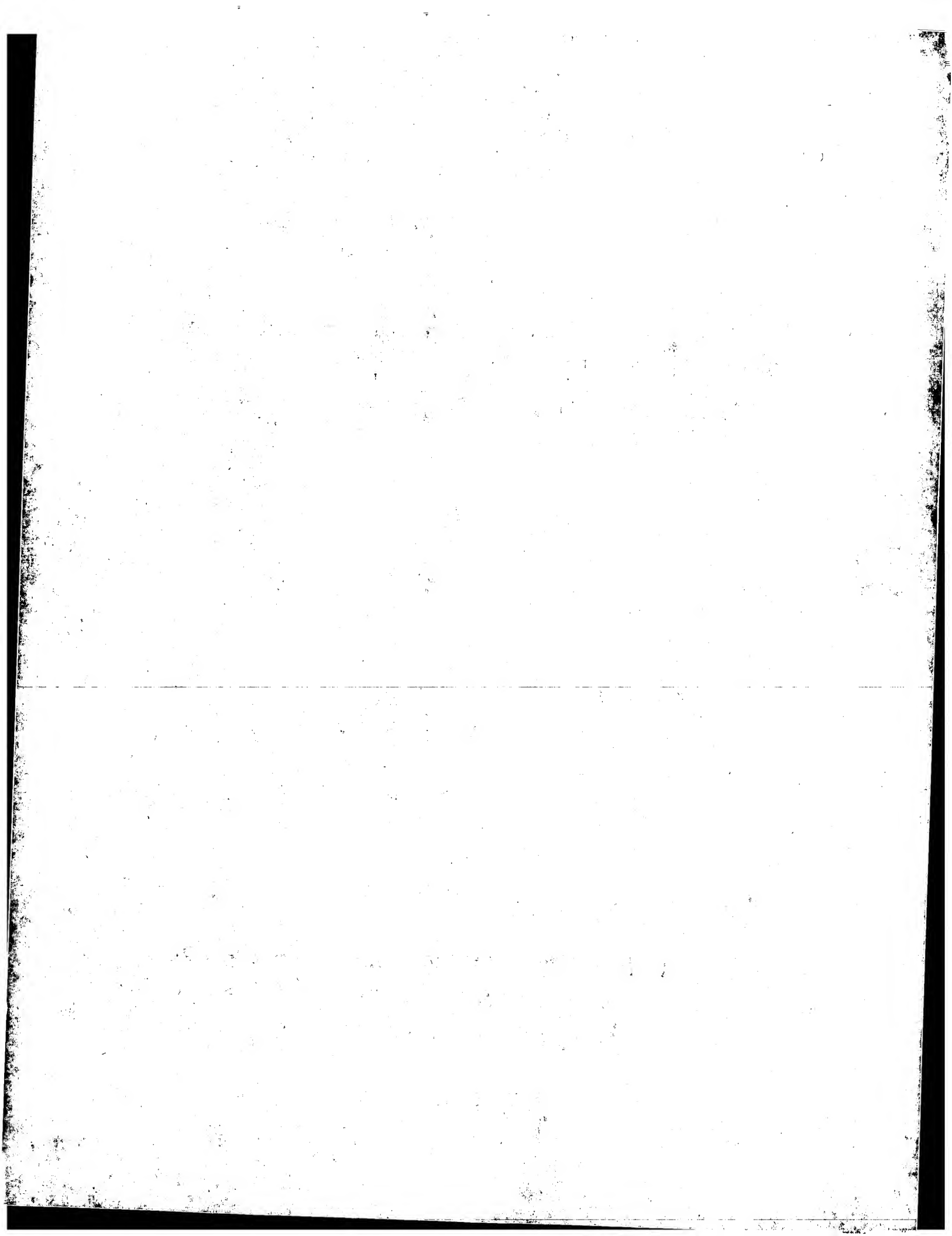
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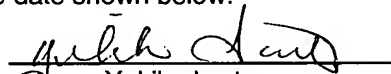
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Yukiko Iwata
Date: April 19, 2004

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of)	
ROBERT AMIN and)	
CASPER K. GROOTHUIS)	
Serial No. 10/772,621)	
Filed February 5, 2004)	
REMOVING CONTAMINANTS FROM)	April 19, 2004
NATURAL GAS)	

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CLAIM TO PRIORITY

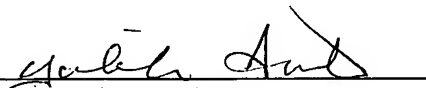
Applicants reaffirm the claim for the benefit of filing date of the following foreign patent application referred to in Applicants' Declaration:

Australian application Serial No. 2003900534 filed February 7, 2003

A copy of the application certified by the Australian Patent Office is enclosed.

Respectfully submitted,

ROBERT AMIN and
CASPER K. GROOTHUIS

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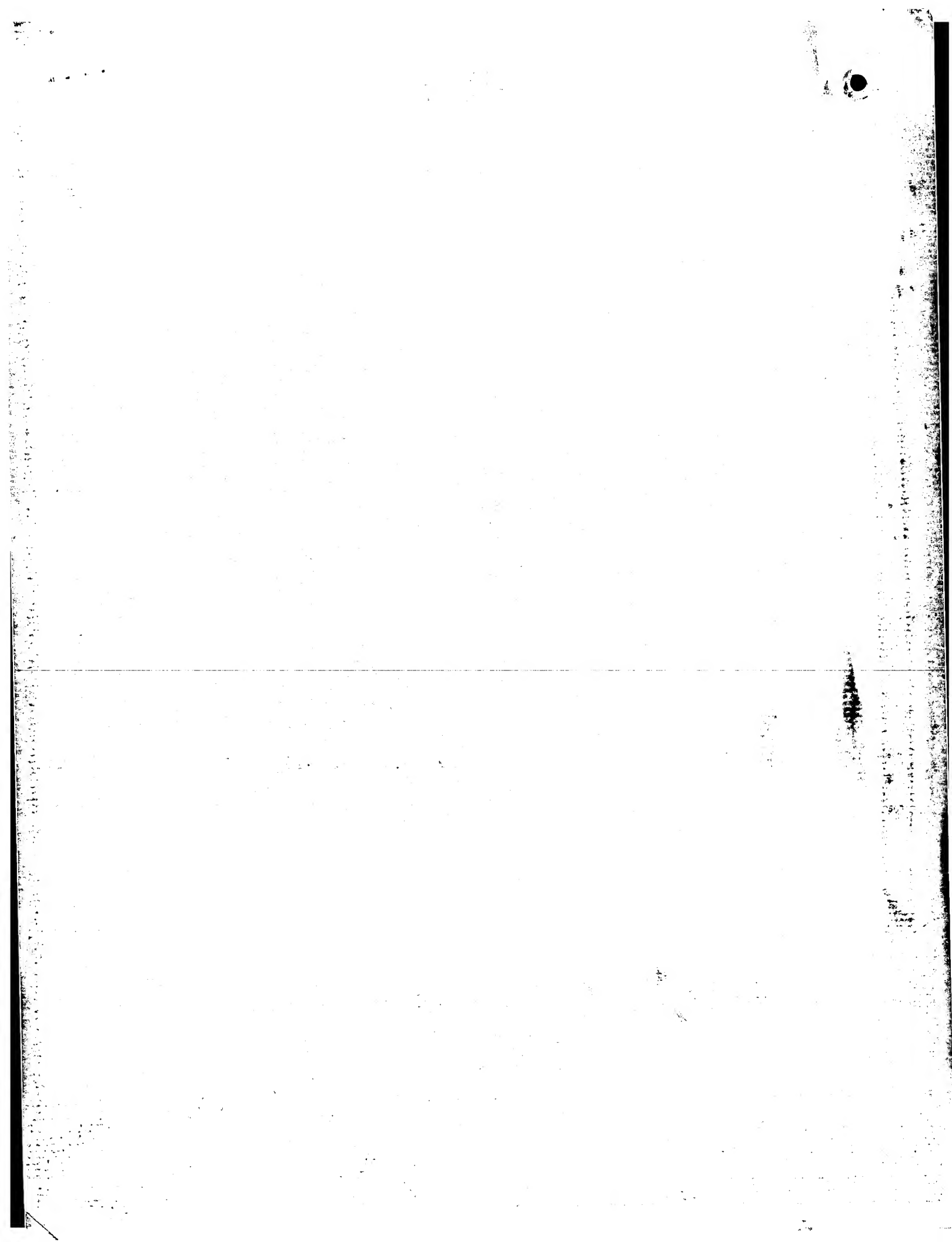
I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003900534 for a patent by CURTIN UNIVERSITY OF TECHNOLOGY and SHELL GLOBAL SOLUTIONS INTERNATIONAL B.V. as filed on 07 February 2003.

I further certify that the above application is now proceeding in the name of SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. pursuant to the provisions of Section 113 of the Patents Act 1990.

WITNESS my hand this
Sixteenth day of February 2004

A handwritten signature in cursive script, appearing to read "J. Billingsley".

JULIE BILLINGSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES



APPLICANT: CURTIN UNIVERSITY OF TECHNOLOGY
and SHELL GLOBAL SOLUTIONS
INTERNATIONAL B.V.

NUMBER:

FILING DATE:

AUSTRALIA

PATENTS ACT 1990

PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:

**"PROCESS AND APPARATUS FOR REMOVAL OF A
CONTAMINANT FROM A NATURAL GAS FEED STREAM"**

The invention is described in the following statement:-

**PROCESS AND APPARATUS FOR REMOVAL OF A CONTAMINANT FROM A
NATURAL GAS FEED STREAM**

Field of the Invention

[0001] The present invention relates to a process and apparatus for removing a contaminant from a natural gas feed stream by forming a solid of the contaminant and subsequently melting the solid contaminant.

[0002] When the contaminant is water, the present invention relates particularly, though not exclusively, to a process and apparatus for dehydrating a natural gas feed stream.

[0003] When the contaminant is hydrogen sulfide, carbon dioxide or both, the present invention relates particularly, though not exclusively, to a process and apparatus for sweetening the natural gas feed stream.

[0004] The present invention also relates particularly, though not exclusively, to a process and apparatus for sequentially dehydrating and sweetening the natural gas feed stream.

Background of the Invention

[0005] Natural gas from either production reservoirs or storage reservoirs typically contains water, as well as other species which form solids during the liquefaction to produce liquefied natural gas (LNG). It is common practice for the natural gas to be subjected to a dehydration process prior to the liquefaction. Water is removed to prevent hydrate formation occurring in pipelines and heat exchangers upstream of the liquefaction vessel.

[0006] If water is not removed, solid hydrates may form in pipework, heat exchangers and/or the liquefaction vessel. The solid hydrates are stable solids comprising water and natural gas having the outward appearance of ice, but with the natural gas stored within the crystal lattice of the hydrate.

[0007] The formation of natural gas hydrates was historically seen as an undesirable result that should be avoided. However, processes have been developed to encourage natural gas hydrate formation such as International Application No. WO 01/00755 and WO 01/12758. In the first of these International applications, a method and apparatus is described whereby natural gas and water are combined in the presence of an agent adapted to reduce the natural gas water interfacial tension to encourage natural gas hydrate formation. In the second of these International applications, a production plant is described, including a convoluted flow path to cause mixing of water and natural gas as a first step prior to reducing the temperature to produce natural gas hydrate.

[0008] Other methods of dehydrating natural gas feed streams known in the art include absorption of water in glycol or adsorption of the water using a solid such as hydrated aluminium oxide, silica gels, silica-alumina gels and molecular sieves.

[0009] Natural gases also typically contain hydrogen sulphide (H_2S) and carbon dioxide (CO_2) and are classified as "sour" gases. When the H_2S and CO_2 have been removed from the natural gas feed stream, the gas is then classified as "sweet". The term "sour gas" is applied to natural gases including H_2S because of the bad odour that is emitted even at low concentrations from an unsweetened gas. H_2S is a contaminant of natural gas that must be removed to satisfy legal requirements, as H_2S and its combustion products of sulphur dioxide and sulphur trioxide are also toxic. Furthermore, H_2S is corrosive to most metals normally associated with gas pipelines so that processing and handling of a sour gas may lead to premature failure of such systems.

[0010] Like dehydration, gas sweetening processes are known in the art and typically include adsorption using solid adsorption processes or absorption using amine processes, molecular sieves, etc. Existing dehydration and gas sweetening processes are extremely complex and expensive.

[0011] The present invention represents an improvement on the process and device disclosed in the applicant's co-pending International Patent Application No. PCT/AU03/00050.

Summary of the Invention

[0012] According to a first aspect of the present invention there is provided a process for removing a contaminant from a natural gas feed stream comprising the steps of:

cooling the natural gas feed stream in a vessel to form solids of the contaminant;

and,

removing from the vessel a stream of treated gas from which the contaminant has been removed.

[0013] Preferably, the step of cooling the feed stream comprises the step of introducing a stream of sub-cooled liquid into the vessel to form a slurry with the solids of the contaminant. The term "sub-cooled" is used throughout this specification to refer to a liquid that has a temperature below the solid/liquid transition temperature for the contaminant at a given pressure of operation of the vessel. The sub-cooled liquid advantageously serves the dual purpose of cooling the feed stream to form solids of the contaminant and assists in washing the solids of the contaminant towards the lowermost portion of the vessel.

[0014] Preferably, the step of introducing the stream of sub-cooled liquid comprises the step of spraying the natural gas feed stream with the stream of sub-cooled liquid introduced to the vessel. More preferably the step of introducing the stream of sub-cooled liquid to the vessel comprises the step of introducing a plurality of streams of sub-cooled liquid to the vessel. More preferably the process comprises the step of spraying the natural gas feed stream with the stream(s) of sub-cooled liquid introduced to the vessel. Spraying is preferred to maximise the contact area between the sub-cooled LNG and the natural gas feed stream so as to achieve maximum efficiency of cooling, and it is preferable that the sprays cover substantially the full cross-sectional area of the vessel.

[0015] Preferably, the process further comprises the step of removing a portion of the slurry of the sub-cooled liquid and the solids of the contaminant from the vessel. More preferably the process further comprises the step of separating the solids of the contaminant from the removed portion of the slurry. More preferably, the step of removing a portion of the slurry from the vessel is conducted simultaneously with the step of separating the solid contaminant from the slurry. Preferably, the process further comprises the step of recycling to the vessel a portion of the sub-cooled liquid from which the solids of the contaminant have been separated.

[0016] Preferably, the sub-cooled liquid is a sub-cooled stream of condensate. Alternatively, the sub-cooled liquid is a sub-cooled stream of LNG. Advantageously, the process further comprises the step of separating condensate from the natural gas feed stream prior to the step of cooling the natural gas feed stream in the vessel. Preferably, the process further comprises the step of cooling the separated condensate to form a sub-cooled liquid stream.

[0017] Preferably, the process further comprises the step of melting the solids of the contaminant. The step of melting may occur within the vessel or external to the vessel. Preferably, the process further comprises the step of melting the solids of the contaminant after the step of removing the solids of the contaminant from the vessel and/or the step of separating the solids of the contaminant from the slurry.

[0018] Alternatively or additionally, the step of melting the solids of the contaminant may occur within the vessel and the contaminant is removed from the vessel as a liquid.

[0019] Preferably, the step of melting comprises the step of adding a warm liquid to the solids of the contaminant. Throughout this specification a "warm" liquid stream can be any compatible stream of liquid having a temperature above the solid/liquid transition temperature of the contaminant for a given pressure of operation of the vessel. The warm liquid stream is thus a temperature that is sufficiently high to cause melting

of the solids of the contaminant. The warm liquid may or may not take the contaminant into solution.

[0020] In one embodiment, the warm liquid is added to the vessel to melt the solids of the contaminant within the vessel. More preferably, the process further comprises the step of forming a mixture of the melted contaminant and the warm liquid. Preferably the process further comprises the step of removing the mixture from the vessel. Preferably, the process further comprises the step of separating the melted contaminant from the mixture of warm liquid and melted contaminant.

[0021] Preferably, the process further comprises the step of recycling to the vessel gas generated during the step of separating the mixture of the melted contaminant from the warm liquid.

[0022] In another embodiment, the step of adding the warm liquid occurs after the step of removing the slurry from the vessel and/or after the step of separating the solids of the contaminant from the slurry. Preferably, the process further comprises the step of recycling to the vessel gas generated during the step of separating the solids of the contaminant from the removed slurry and/or the step of melting the solids of the contaminant after the step of separating the solids of the contaminant from the removed slurry.

[0023] The preferred warm liquid is condensate present in the natural gas feed stream, as warm condensate is readily available in a typical natural gas plant. One source of warm condensate may be a portion of the condensate separated from the natural gas feed stream prior to the step of cooling in the vessel.

[0024] The warm liquid can be used to melt the solids of the contaminant either by direct contact of the solids of the contaminant with the warm liquid or by indirect heating of the solids of the contaminant with the warm liquid; for example, using a suitably arranged heat exchanger.

[0025] Preferably, the process further comprises the step of cooling a portion of the warm liquid to form a stream of sub-cooled liquid.

[0026] Preferably, the step of cooling is conducted in a manner such that the solids of the contaminant form preferentially away from the wall of the vessel. One way of promoting the formation of the solidification of the contaminant away from the walls of the cooling vessels is to maintain a temperature gradient within the vessel such that the temperature towards the centre of the vessel is less than the temperature at the wall of the vessel. In practice, one way of achieving this is to use a material of construction for at least a portion of the internal wall of the cooling vessel surrounding the solidification zone from a material having a low thermal conductivity. Throughout this specification the term "solidification zone" is used to describe the zone within the vessel within which solids of the contaminant form during the step of cooling.

[0027] Preferably, the process further comprises the step of cooling the sweetened gas to form LNG downstream of the vessel.

[0028] Preferably, the step of cooling further comprises the step of isotropically expanding the feed stream.

[0029] Preferably, the contaminant is water and the step of cooling is conducted under hydrate forming conditions to produce a dry natural gas.

[0030] Alternatively, the contaminant(s) are sour gas species and the step of cooling is conducted under conditions suitable to the formation of solids of the sour gas species. The term "sour gas species" is used throughout this specification to refer to hydrogen sulphide and/or carbon dioxide. Preferably the process further comprises the step of cooling the sweetened gas to form LNG downstream of the vessel.

[0031] As a further alternative, the step of cooling is conducted under LNG forming

conditions to form solids of the freezable species. Throughout this specification, the term "freezable species" refers to any species that forms solids under the temperature-pressure conditions that are conducive to liquefaction of the natural gas. The freezable species include, but are not limited, to hydrogen sulphide, carbon dioxide, mercury and heavy hydrocarbons such as butane, toluene, ethylbenzene and xylene. Thus the sour gas species form a subset of the freezable species. In this embodiment the process further comprises the step of removing from the vessel a product stream of sweetened natural gas and a product stream of LNG from which the solidified contaminants have been removed.

[0032] According to a second aspect of the present invention there is provided a process for treating a natural gas feed stream comprising the steps of:

- (a) cooling the natural gas feed stream in a first vessel under hydrate forming conditions to form hydrates and removing a stream of dehydrated gas from the first vessel; and,
- (b) cooling the dehydrated gas in a second vessel to form solids of the sour gas species and removing from the vessel a stream of dry sweetened gas.

[0033] Preferably, the process further comprises the step of cooling the dehydrated gas to form solids of the freezable species and removing from the vessel a stream of LNG and sweetened gas. Alternatively, the process further comprises the step of cooling the dry sweetened gas in a third vessel to form solids of the freezable species and removing a stream of LNG.

[0034] According to a third aspect of the present invention, there is provided an apparatus for the continuous removal of a contaminant from a natural gas feed stream comprising:

- a natural gas feed stream inlet for introducing the natural gas feed stream;
- a vessel for receiving the natural gas feed stream and cooling the natural gas feed stream to form solids of the contaminant; and,

a gas outlet for removing from the vessel a stream of treated gas from which the contaminant has been removed.

[0035] Preferably, the apparatus further comprises means for introducing a stream of sub-cooled liquid into the vessel to form a slurry with the solids of the contaminant. More preferably, the apparatus further comprises means for introducing a plurality of streams of sub-cooled liquid into the vessel. The means for introducing the stream(s) of sub-cooled liquid may be a plurality of nozzles, each nozzle producing a mist or spray of liquid in the first region. The nozzles are typically positioned so as to be located at a height within an uppermost portion of the vessel. More preferably, the nozzles are located above the height of the natural gas feed stream inlet. Preferably, the nozzles are above the lowermost portion of the gas outlet. In a typical embodiment, the nozzles are arranged around a periphery of the vessel.

[0036] Preferably, the apparatus further comprises a first outlet for removing a portion of the slurry of the sub-cooled liquid and the solids of the contaminant from the vessel. More preferably, the first outlet includes or is defined by means for separating the solids of the contaminant from the slurry.

[0037] Preferably, the apparatus further comprises a gas/condensate separator with the preferred gas/condensate separator being a flash tank.

[0038] Preferably, the apparatus further comprises means for melting the solids of the contaminant. More preferably, the means for melting the solids of the contaminant is integral with the vessel. Alternatively, the apparatus further comprises means for transferring the solids of the contaminant from the vessel to a means for melting external to the vessel. In either case, the preferred means for melting is a reboiler.

[0039] Preferably, the natural gas feed stream inlet comprises means for expanding the natural gas feed stream. In one embodiment, the means for expanding is a Joule-

Thompson valve. Expanding the gas in this way assists in cooling the feed stream for liquefaction of LNG.

[0040] The gas outlet may include means for increasing the residence time in the vessel so as to maximise the potential for solids of the contaminant to form before the gas exits the vessel. In one embodiment, the gas outlet is in the form of a pipe and the means for increasing the residence time includes extending the pipe into an uppermost region of the vessel to a distance not greater than the height of the natural gas feed stream inlet.

[0041] Preferably, the apparatus comprises a transfer means for passing the solids from the vessel to the means for melting. The transfer means is preferably a pipe with a cross-sectional area less than the cross-sectional area of the vessel so as to restrict the flow of the solids from the vessel to the means for melting. Preferably, the transfer means further comprises a choke having a variable cross-sectional area for adjustably controlling the cross-sectional area thereof. Alternatively, the transfer means may be in the form of an S-bend pipe configuration which, once filled with the slurry, prevents the transfer of natural gas vapour from the means for melting to the vessel.

[0042] The transfer means is typically configured to maintain a liquid level of the slurry in the vessel to allow sufficient residence time for the solids of the contaminant to migrate under gravity towards the lowermost region of the vessel.

[0043] Preferably, that part of the wall of the vessel that surrounds the area in which solids of the contaminant form within the vessel is constructed from a material having a low thermal conductivity. It is possible for the entire vessel to be constructed of a material having a low thermal conductivity. Preferably, the internal wall of the vessel surrounding the area in which solids form within the vessel is constructed of a material having a low thermal conductivity. Thus, the vessel may have an outer housing constructed of a material having a high thermal conductivity with the internal part of the

vessel that surrounds the first region being constructed of a material having a low thermal conductivity.

[0044] One of the advantages of employing a material having a low thermal conductivity is that a thermal gradient can be developed within the cooling vessel whereby the temperature towards the centre of the cooling vessel can be maintained at all times cooler than the temperature at the wall(s) of the cooling vessel. The outcome is that the contaminants solidify preferentially towards the centre of the vessel, avoiding the problems associated with solidification on the walls of the vessel. Fouling of the vessel is thus reduced or eliminated, thereby reducing the time during which the vessel needs to be taken off-line.

[0045] Preferably, the material of construction of an internal wall of the first region is polished and is, more preferably, highly polished.

[0046] Preferably, the material of construction of the internal wall of the first region of the vessel is anisotropic. The material of construction may be a metal oxide or a ceramic. More preferably, the material of construction is a single crystal. One suitable material of construction is sapphire.

[0047] According to a fourth aspect of the present invention there is provided an apparatus for treating a natural gas feed stream, the apparatus comprising:

a first vessel for cooling the natural gas feed stream under hydrate forming conditions to form hydrates and produce a stream of dehydrated gas; and

a second vessel for receiving the stream of dehydrated gas and cooling the dehydrated gas to form solids of the sour gas species and produce a stream of dry sweetened gas.

Brief Description of the Drawings

[0048] Preferred embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a flow sheet illustrating a first embodiment of the process and apparatus according to the present invention used for gas sweetening and dehydration;

Figure 2 is a flow sheet illustrating a second embodiment of the process and apparatus according to the present invention used for gas sweetening and dehydration;

Figure 3 is a pressure-temperature phase diagram for CO₂;

Figure 4 illustrates a first preferred embodiment of a vessel for use in the process and apparatus of the present invention;

Figure 5 illustrates a second preferred embodiment of a vessel for use in the process and apparatus of the present invention;

Figure 6 illustrates a third preferred embodiment of a vessel for use in the process and apparatus of the present invention; and,

Figure 7 illustrates a fourth preferred embodiment of a vessel for use in the process and apparatus of the present invention.

Detailed Description of the Preferred Embodiments of the Invention

[0049] With reference to Figure 1 and Figure 2, two preferred embodiments are described below. In each of the embodiments illustrated in Figures 1 and 2 there is provided an apparatus 10 comprising a first vessel 12 and a second vessel 14. The contaminant removed in the first vessel 12 is water and thus the gas exiting the first vessel 12 is dry. The dry gas is sweetened in the second vessel 14. In the first preferred embodiment as illustrated in Figure 1, LNG is produced in the second vessel and thus two potential product streams are available, namely sweetened gas and LNG, with both products being substantially free of freezable species. In the second preferred embodiment of the present invention, the second vessel is used to sweeten the dry gas without forming LNG. The contaminants removed as solids in the second vessel are thus the sour gas species.

[0050] In the first preferred embodiment as illustrated in Figure 1, sour wet feed gas from a well head is fed to a first flash tank 16 in which the condensate is separated from the gas. The pressure and temperature conditions within the first flash tank 16 would typically be in the order of 75 bar and 25°C. The condensate stream exiting the first

flash vessel 16 is "a warm liquid" as defined above. The warm condensate from the first flash tank 16 enters the first vessel 12 via warm condensate inlet 18. The gas stream separated from the sour wet feed gas in the first flash tank 16 enters the first vessel 12 via wet sour gas feed stream inlet 20. An intermediate heat exchanger 22 may be used to cool the wet sour gas between the first flash tank 16 and the first vessel 12. The intermediate heat exchanger 22 drops the temperature of the wet sour gas to a temperature just above the hydrate formation temperature for the particular line pressure of this feed stream.

[0051] The wet sour gas feed stream fed to the first vessel 12 is expanded using a Joule-Thompson valve 24 or other suitable expansion means such as a turbo expander to further cool the stream as it enters the first vessel 12. The Joule-Thompson valve 24 may alternatively define the inlet 20 to the first vessel 12. Upon expansion of the wet sour gas feed stream into the first vessel 12, the gas pressure-temperature conditions within the vessel 12 allow hydrates to form. The necessary degree of cooling is achieved either by the degree of expansion of the wet sour gas feed stream through the Joule-Thompson valve 24 or through cooling of the natural gas feed stream using one or more sprays of a sub-cooled liquid introduced via sub-cooled liquid inlet 26 or both.

[0052] The sub-cooled liquid inlet 26 should be located at a height within the first vessel 12 that is higher than the wet sour gas feed stream inlet 20. In the illustrated embodiments, the sub-cooled liquid inlet 26 is a plurality of spray nozzles. The particular sub-cooled liquid is condensate recycled from the process and sprayed into the first vessel. Sprays are used in order to maximise the contact area of the sub-cooled liquid and the gas and thus the cooling effect of contact of the sub-cooled liquid with the wet sour gas.

[0053] The temperature and pressure conditions within the first vessel 12 are maintained at a level whereby solids of H_2S and CO_2 of the freezable species do not also form in the first vessel.

[0054] A portion of the stream of warm condensate separated using the first flash tank 16 is fed to the first vessel 12 via inlet 18 and is sufficiently warm to liquefy hydrate formed in the first region of the first vessel 12. As the hydrates melt, the gas trapped in the hydrate lattice is liberated and the water goes into solution with the condensate. A water/condensate stream is removed from the first vessel 12 via water condensate outlet 28. The water is separated from the condensate using a water condensate separator 30; for example, a baffled gravity separation unit. As water is heavier than the condensate, any suitable gravity separation techniques may be used. The separated condensate or at least a portion thereof may then be recycled for use as the warm liquid used for heating the solids of the freezable species in the second vessel. Alternatively or additionally, a portion of the condensate stream from the water/condensate separator 30 may be recycled to the warm condensate inlet 18 of the first vessel 12.

[0055] Any gas present within the water condensate separator 30 may be recycled to the first vessel 12 via gas balancing inlet 32. Alternatively or additionally, a portion of the gas separated in the water/condensate separator 30 may be recycled to the wet sour gas feed stream entering the first vessel 12 via inlet 20.

[0056] The dry sour gas exits the first vessel 12 via dry sour gas outlet 34. Typically the dry sour gas exiting the first vessel 12 would have a nominal pressure of 65 bar at a temperature of 5°C. The dry sour gas stream may be cooled using a second heat exchanger 36 to a temperature greater than that at which the solids of the freezable species form for the given line pressure. At a nominal pressure of 65 bar, the dry sour gas is cooled to a temperature of around -56°C by using the second heat exchanger 36.

[0057] In the illustrated embodiment of Figure 1, the cooled dry sour gas is directed via a reboiler 38 to a second flash tank 40.

[0058] In the second flash tank 40, condensate is separated from the dry sour gas stream. The condensate stream exits the second flash tank 40 via condensate outlet 42 and is sufficiently cooled to satisfy the criteria of a sub-cooled liquid that may be fed to the sub-

cooled liquid inlet 26 of the first vessel 12.

[0059] The dry sour gas exits the second flash tank 40 via gas outlet 44 and is fed to the second vessel 14 via dry sour gas inlet 46. As with the first vessel, the dry sour gas being fed to the second vessel may be expanded through a Joule-Thompson valve 48 or other suitable expansion means, such as a turbo expander, in order to further cool the gas. As before with the first vessel, the Joule-Thompson valve may define the dry sour gas inlet 46.

[0060] A stream of sub-cooled liquid is introduced to the second vessel via sub-cooled liquid inlet 48 located at a height greater than the height of the dry sour gas inlet 46. One or more sprays of the sub-cooled liquid entering through the sub-cooled liquid inlet 48 to the second vessel 14 is used to further cool the dry sour gas stream entering the second vessel 14. The temperature and pressure conditions within the second vessel are adjusted so as to form solids of the freezable species. For sweetening of a gas, the temperature-pressure conditions need only be adjusted to form solids of hydrogen sulphide (H_2S) and carbon dioxide (CO_2). However, if the process conditions within the second vessel are sufficient to cause the formation of liquefied natural gas, solids of the freezable species of other hydrocarbons such as benzene, toluene, ethylbenzene and xylene may also form within the second vessel 14.

[0061] The solids of the freezable species migrate under gravity towards a lowermost portion of the second vessel 14. The spray of the sub-cooled liquid introduced via sub-cooled liquid inlet 48 assist in washing the solids of the freezable species towards the lowermost portion of the second vessel 14. The lowermost portion of the second vessel 14 is provided with two outlets: a condensate outlet 50 for removing a stream of condensate to be recycled to the sub-cooled liquid inlet 48 and a second outlet 52 for removing a stream of condensate, including the freezable species either in solid or liquid form.

[0062] In the illustrated embodiment of Figure 1, a slurry of the solids of the freezable species and condensate is removed via second outlet 52 and is transferred via a transfer

means 54 to a reboiler 38. In the illustrated embodiment of Figure 1 the transfer means 54 is separate to the second vessel 14. The applicant's co-pending provisional patent application entitled "Process and apparatus for continuous removal of a contaminant from a natural gas feed stream" filed on the same day as the present application and incorporated herein by reference teaches a single vessel incorporating the transfer means 54 and reboiler as an integral part of the second vessel 14.

[0063] In the reboiler 38, the solids of the freezable species are converted to liquid form. The dry sour gas stream exiting the first vessel 34 may be used as a source of heat to the reboiler 38, as may any of the other warm process streams. The gas vapour generated in the reboiler 38 may be recycled to the second vessel 14 via gas balancing inlet 60. Alternatively, the vapour stream from the reboiler 38 may be added to the dry sour gas feed stream entering the second vessel 14 via dry sour gas inlet 46.

[0064] An alternative means for melting according to a second preferred embodiment of the present invention is illustrated in Figure 2. In this embodiment, a portion of a condensate stream from the water/condensate separator 30 is fed to a warm condensate inlet 56 to liquefy the solids of the freezable species within a second region of the second vessel 14. The melted freezable species form a mixture with the condensate in the second region of the second vessel 14 and the mixture of the liquefied freezable species and the condensate is removed from the second vessel 14 via outlet 52.

[0065] The gas exiting the second vessel 14 via outlet 62 is dehydrated and sweetened. The dry sweetened gas would typically be at a pressure of around 50 bar and a temperature of around -62°C . This product stream of sweetened dry gas is typically transported to the end user at ambient temperature. The product stream of dry sweetened gas may thus be used in one or more of the heat exchangers 22 or 36 to effect cooling of one or more of the other process streams within the apparatus 10.

[0066] Preferred embodiments of suitable vessels are illustrated in Figures 4 to 7 wherein like numerals refer to like parts based on the description of the preferred

embodiments of the present invention described above. Figure 4 illustrates the vessel described in the applicants' co-pending provisional patent application entitled "Process and apparatus for continuous removal of a contaminant from a natural gas feed stream" filed on the same day as the present application and incorporated herein by reference. The vessel of Figure 4 would be particularly suited for use as the second vessel 14 in the illustrated embodiment of Figure 1.

[0067] With reference to Figure 4, the second vessel 14 has a first region 120, second region 140 and a transfer means 160 provided between the first region 120 and second region 140. A dry gas stream is introduced to the first region 120 of the second vessel 14 through dry gas inlet 46 defined by a Joule-Thompson valve 48 for isotropically expanding and thus cooling the dry gas as it enters the second vessel 14.

[0068] The temperature and pressure conditions of the dry gas stream prior to entry into the second vessel 14 should be maintained such that solids of, in this case, the sour gas species do not form upstream of the vessel. Once the natural gas feed stream is introduced to the first region 120 of the second vessel 14 via dry gas inlet 46, the gas is cooled in the first region 120 to form a slurry of the solids of the sour gas species in the sub-cooled liquid. One or more streams of sub-cooled liquid is sprayed into the first region 120 of the vessel using spray nozzles 48.

[0069] The solids of the sour gas species within the slurry migrate under gravity to the lowermost portion of the first region 120 of the vessel. The sprays assist in washing the solids towards the lowermost portion of the first region 120.

[0070] As illustrated in Figure 4, the first region 120 further comprises a sweet gas outlet 62 having a tube 320 which extends from the uppermost portion of the first region 120 to a level higher than the level of the dry gas inlet 46. Using a tube that extends into an intermediate position within the first region 120 of the vessel increases the residence time of the gas within the first region in order to maximise the efficiency of sweetening. In the absence of using such a tube or pipe, the natural gas feed stream may enter the

first region 120 of the vessel 11 via dry gas inlet 46 and exit the vessel at the sweet gas outlet 62 without sufficient residence time within the first region 120 of the vessel 11 for sweetening to occur.

[0071] Other means for increasing the residence time of the natural gas feed stream in the first region 120 may be used instead of the tube illustrated in Figure 2. Such means could include a configuration of baffle plates or a conical housing arrangement.

[0072] As described in greater detail below in relation to the vessels depicted in Figures 5-7, the material of construction of at least that part of the internal wall of the vessel in the area of the first region 120 is a material of low thermal conductivity such as titanium, partially stabilised zirconia, sapphire or other suitable ceramic material. The particular material chosen should be able to withstand the process conditions of pressure and temperature required to perform liquefaction of the natural gas and have a sufficiently low thermal conductivity such that the temperature towards the centre of the first region of the vessel is less than the temperature at the walls of the first region 120 of the vessel. One material that has proved particularly successful is highly polished titanium, while another that has proved successful is highly polished single crystal sapphire.

[0073] The slurry is transferred from the first region 120 to the second region 140 via transfer means 160 in the form of a restrictor 400 in the illustrated embodiment of Figure 1. The restrictor 400 has a cross-sectional area less than that of the first and second regions of the vessel 14 and may include means for varying the cross-section; for example, a variable choke (not illustrated). Alternatively, the restrictor 400 may be in the form of a convoluted pipe or S-bend.

[0074] The restrictor 400 serves two purposes. Firstly, the degree of resistance afforded by the restrictor 400 to the flow of the slurry from the first region 120 to the second region 140 governs the residence time of the slurry within the first region 120. The residence time of the slurry within the first region 120 of the vessel 14 also governs

the degree of separation of the solids of the sour gas species within the slurry. With increased residence time, the lowermost portion of the slurry becomes more concentrated in solids.

[0075] The restrictor 400 also serves the purpose of preventing gas or vapour from moving from the second region 140 to the first region 120 by providing a liquid barrier between the first and second regions.

[0076] In the second region 140, the solids of the sour gas species within the slurry are melted under temperature and pressure conditions such that a vapour phase of the sour gas species is avoided. In the illustrated embodiment of Figure 4, the means for melting the solids of the sour gas species is a reboiler 38. Alternatively, a stream of warm liquid may be used to melt the solids in the second region 140 to form a mixture of warm liquid and the liquefied sour gas species. In Figure 4, a liquid stream of the sour gas species is removed from the second region 140 of the vessel via first outlet 440. In the illustrated embodiment of Figure 4, the first outlet 440 is located at the lowermost portion of the second region 140 and defines the exit of the reboiler 38. The liquefied stream of the freezable species may be used downstream of the vessel 14 for other purposes, eg in one or more heat exchangers.

[0077] During the step of heating the slurry in the reboiler so as to melt the solids of the sour gas species, natural gas vapour is generated and a portion of this gas may be recycled to the first region of the vessel via gas return inlet 60. The gas return stream passes through a non-return valve 500 which remains open at all times to allow gas to pass from the second region 140 via inlet 60 to the first region 120.

[0078] In use, the pressure in the first region 120, the second region 140 and transfer means 160 would be maintained at the same level. The pressure-temperature conditions would also be regulated so as to avoid the formation of a vapour of the sour gas species.

[0079] Figures 5 to 7 illustrate other preferred embodiments of a vessel for use in the process and apparatus of the present invention based on the vessels described in the applicant's co-pending International Patent Application No. PCT/AU03/00050.

[0080] The portion of the vessel in which solids of the contaminant form during the step of cooling is herein defined as the "solidification zone". In the preferred embodiments of the vessels as depicted in each of Figures 5 to 7, the solidification zone within the vessel is effectively an open space within the cooling vessel with no trays or plates or other physical barriers of any kind. The material of construction of at least that part of the internal wall of the vessel in the area of the solidification zone may be of any material able to withstand the process conditions of pressure and temperature required to form solids of the particular contaminant being removed provided that the material has a sufficiently low thermal conductivity that the temperature is at all times cooler towards the centre of the vessel than the temperature at the wall of the vessel in the solidification zone.

[0081] Such a choice of materials of construction for the cooling vessel is a radical departure from convention material selection practice for liquefaction of natural gas. Selecting the material of construction having a low heat transfer coefficient for at least that part of the cooling vessel that surrounds the solidification zone results in a thermal gradient within the vessel whereby the temperature towards the centre of the vessel is at all times cooler than the temperature at the walls of the vessel. The contaminant will then preferentially form solids away from the wall of the vessel surrounding the solidification zone due at least in part to the thermal gradient being maintained such that the temperature towards the centre of the vessel is at all times less than the temperature at the walls.

[0082] The prototype vessel constructed by the applicant for testing of the present invention was constructed of highly polished synthetic single crystal sapphire. Sapphire was chosen in order to provide a means for observing the formation of solids of the contaminants during cooling. A surprising outcome of the observations was that the

choice of single crystal sapphire as the material of construction resulted in the solids forming away from the walls of the vessel. It is to be clearly understood, however, that the present invention is not limited in its scope to the selection of sapphire as the material of construction of the cooling vessel. Any other suitable material having a low heat transfer coefficient is sufficient. Such a material may be a metal oxide or a ceramic such as partially stabilised zirconia or other metals such as titanium.

[0083] The particular material of construction used during testing had a high level of anisotropy. Without wishing to be bound by theory, an anisotropic growth habit is understood to have been one of the other factors that contributed to discouraging solids formation occurring at the walls of the cooling vessel. Additionally, the single crystal sapphire was highly polished and a polished sapphire surface is ranked as one of the smoothest known amongst any material. It is considered that polishing of at least the internal surface of the material of construction of the wall in the solidification zone is one of the factors that contributes to solids forming preferentially away from the walls of the cooling vessel.

[0084] It is understood that yet another factor encouraging solid formation to occur away from the walls of the cooling vessel is the differential surface tension that arises due to the thermal gradient that is induced within the cryogenic liquid. A liquid at a lower temperature is known to have a higher surface tension than a liquid at a higher temperature. By constructing at least part of the wall surrounding the solidification zone from a material having a low heat transfer coefficient, the temperature towards the centre of the vessel and thus the surface tension of the sub-cooled liquid present towards the centre of the vessel is higher. Again, the formation of solids towards the centre of the cooling vessel is encouraged to reduce the overall energy of the system.

[0085] The vessels illustrated in Figures 5 to 7 are equally suited for use as either the first vessel 12 or second vessel 14 or both in the preferred embodiments illustrated in Figures 1 and 2.

[0086] With reference to Figure 5 and describing the use of the vessel depicted in Figure 5 as the first vessel 12 in the illustrated embodiment of Figure 1, a wet sour gas is expanded into the first vessel 12 through a Joule-Thompson valve 24. When the first vessel 12 is operated under hydrate forming conditions, solid hydrates form within the vessel 12. A stream of sub-cooled liquid 26 is sprayed into the first vessel 14 in the usual manner. Upon contact with the sub-cooled liquid mist, solids of hydrate form within the solidification zone of the first vessel 12 forming a slurry with the sub-cooled liquid. The solid hydrates are more dense than the sub-cooled liquid and thus migrate under gravity towards the lowermost portion of the vessel 12 at which the outlet 28 is located.

[0087] A second stream of sub-cooled liquid or warm condensate may be injected into the first vessel through an inlet 80 adapted to be tangential to and located near a top portion of the slurry to create the vortex within the slurry. The creation of a vortex is understood to assist in accumulating solids of the contaminant, in this case hydrates towards the centre of the vessel. The vortex is also understood to encourage the migration of the solids of the contaminants under gravity towards the outlet 28.

[0088] Another method of creating a vortex is to provide a stirrer or other suitable mechanical agitation means (not shown) towards the lowermost portion of the vessel.

[0089] In the preferred embodiment illustrated in Figure 5 used as the first vessel in the process illustrated in Figure 1, the slurry of hydrates and sub-cooled liquid is removed from the first vessel 12 via outlet 28. The solid hydrates are separated from the slurry using a solid/liquid separator 82 such as a hydrocyclone. One or more cyclones 82 in series or parallel may also be employed downstream of the first vessel 12. Alternatively, the solid/liquid separator 82 defines the outlet 28 and is an integral part of the first vessel 12.

[0090] The preferred embodiment illustrated in Figure 6 may be used as either the first or second vessel in the illustrated embodiments of Figures 1 or 2. In use, the description

to follow, the vessel of Figure 6 is used as the second vessel in the preferred embodiment illustrated in Figure 1. For the purposes of the discussion of Figure 6, the natural gas is being cooled to cause liquefaction and thus solids of the freezable species are melted in the second vessel 14 using a stream of warm condensate fed into the second vessel 14 via warm condensate inlet 77.

[0091] In Figure 7, the second vessel 14 includes a hydrocyclone as the outlet 52 through which the slurry exits the second vessel 14. The slurry is then transferred using transfer means 54 in the form of a screw conveyor to reboiler 38 in which the solids of the freezable species are melted. Any suitable means for transferring of the slurry from the second vessel 14 to the means for melting 38 may be employed, such as an incline screw conveyor, an auger or standard conveyor.

[0092] The reboiler 38, transfer means 54 and the second vessel 14 are in fluid communication with each other. In use, the reboiler 38, transfer means 54 and the second vessel 14 are maintained at the same pressure to allow the vessel to be operated on a continuous basis. It is highly desirable that pressure be regulated for a given temperature within each of the second vessel and reboiler to avoid forming a vapour of the contaminant.

[0093] In the preferred embodiment as illustrated in Figure 7, the screw conveyor 54 is mounted at an angle to assist in the draining of sub-cooled LNG from the slurry. Typically the angle of inclination of the screw conveyor 54 is in the order of 60°. The slurry would typically be transferred to a height greater than the height of the slurry within the second vessel 14 to assist in draining the sub-cooled LNG during the transfer.

[0094] The slurry is heated in the reboiler 38 to melt the solids of the freezable species. A liquid stream of the freezable species may then be removed from the reboiler 38.

[0095] Alternatively, the slurry may be melted by introducing a stream of warm liquid

to the reboiler 38. In this case, a further separator (not shown) may be used to separate the warm liquid from the melted solids of the freezable species.

[0096] During the step of melting of the solids of the freezable species, a gas stream is produced and this may be recycled to the second vessel via gas return inlet 60.

[0097] The reboiler 38 may include a stirrer (not shown) to avoid forming hot spots during melting.

[0098] Numerous variations and modifications will suggest themselves to persons skilled in the relevant art, in addition to those already described, without departing from the basic inventive concepts. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the foregoing description.

Claims defining the Invention

1. A process for removing a contaminant from a natural gas feed stream comprising the steps of:
cooling the natural gas feed stream in a vessel to form solids of the contaminant;
and,
removing from the vessel a stream of treated gas from which the contaminant has been removed.
2. A process as defined in claim 1 wherein the step of cooling the feed stream comprises the step of introducing a stream of sub-cooled liquid into the vessel to form a slurry with the solids of the contaminant.
3. A process as defined in claim 2 wherein the step of introducing the stream of sub-cooled liquid comprises the step of spraying the natural gas feed stream with the stream of sub-cooled liquid introduced to the vessel.
4. A process as defined in any one of the preceding claims further comprising the step of removing a portion of the slurry of the sub-cooled liquid and the solids of the contaminant from the vessel.
5. A process as defined in claim 4 further comprising the step of separating the solids of the contaminant from the removed portion of the slurry.
6. A process as defined in any one of the preceding claims further comprising the step of melting the solids of the contaminant.
7. A process as defined in claim 6 wherein the step of melting is conducted within the vessel.
8. A process as defined in claim 6 or claim 7 wherein the step of melting comprises the step of adding a warm liquid to the solids of the contaminant to form a mixture of

the warm liquid and melted solids of the contaminant.

9. A process as defined in claim 8 further comprising the step of removing the mixture from the vessel.

10. A process as defined in claim 9 further comprising the step of separating the warm liquid from the mixture.

11. A process as defined in any one of the preceding claims further comprising the step of maintaining a temperature gradient within the vessel such that the temperature towards the centre of the vessel is less than the temperature at the wall of the vessel.

12. A process for treating a natural gas feed stream comprising the steps of:

(a) cooling the natural gas feed stream in a first vessel under hydrate forming conditions to form hydrates and removing a stream of dehydrated gas from the first vessel; and,

(b) cooling the dehydrated gas in a second vessel to form solids of the sour gas species and removing from the vessel a stream of dry sweetened gas.

13. A process as defined in claim 12 further comprising the step of cooling the dehydrated gas to form solids of the freezable species and removing from the vessel a stream of LNG and sweetened gas.

14. An apparatus for the continuous removal of a contaminant from a natural gas feed stream comprising:

a natural gas feed stream inlet for introducing the natural gas feed stream;

a vessel for receiving the natural gas feed stream and cooling the natural gas feed stream to form solids of the contaminant; and,

a gas outlet for removing from the vessel a stream of treated gas from which the contaminant has been removed.

15. An apparatus as defined in claim 14 further comprising means for introducing a stream of sub-cooled liquid into the vessel to form a slurry with the solids of the contaminant.
16. An apparatus as defined in claim 14 or claim 15 further comprising a first outlet for removing a portion of the slurry of the sub-cooled liquid and the solids of the contaminant from the vessel.
17. An apparatus as defined in any one of claims 14 to 16 further comprising means for melting the solids of the contaminant.
18. An apparatus as defined in claim 18 further comprising means for transferring the solids of the contaminant from the vessel to a means for melting external to the vessel.
19. An apparatus as defined in any one of claims 14 to 18 further comprising means for increasing the residence time in the vessel
20. An apparatus as defined in claim 19 wherein the means for increasing the residence time extends from an uppermost region of the vessel to a distance not greater than the height of the natural gas feed stream inlet.
21. An apparatus as defined in any one of claims 14 to 20 wherein that part of the wall of the vessel that surrounds the area in which solids of the contaminant form within the vessel is constructed from a material having a low thermal conductivity.
22. An apparatus as defined in claim 21 wherein the material of construction of an internal wall of the first region is polished.
23. An apparatus as defined in claims 21 or 22 wherein the material of construction of the internal wall of the first region of the vessel is anisotropic.

24. An apparatus as defined in any one of claims 21 to 23 wherein the material of construction may be a metal oxide or a ceramic.

25. An apparatus as defined in any one of claims 21 to 24 wherein the material of construction is a single crystal.

26. An apparatus for treating a natural gas feed stream, the apparatus comprising:
a first vessel for cooling the natural gas feed stream under hydrate forming conditions to form hydrates and produce a stream of dehydrated gas; and
a second vessel for receiving the stream of dehydrated gas and cooling the dehydrated gas to form solids of the sour gas species and produce a stream of dry sweetened gas.

Dated this 7th day of February 2003

CURTIN UNIVERSITY OF TECHNOLOGY and
SHELL GLOBAL SOLUTIONS INTERNATIONAL B.V.

By Its Patent Attorneys

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Attorneys of Australia.

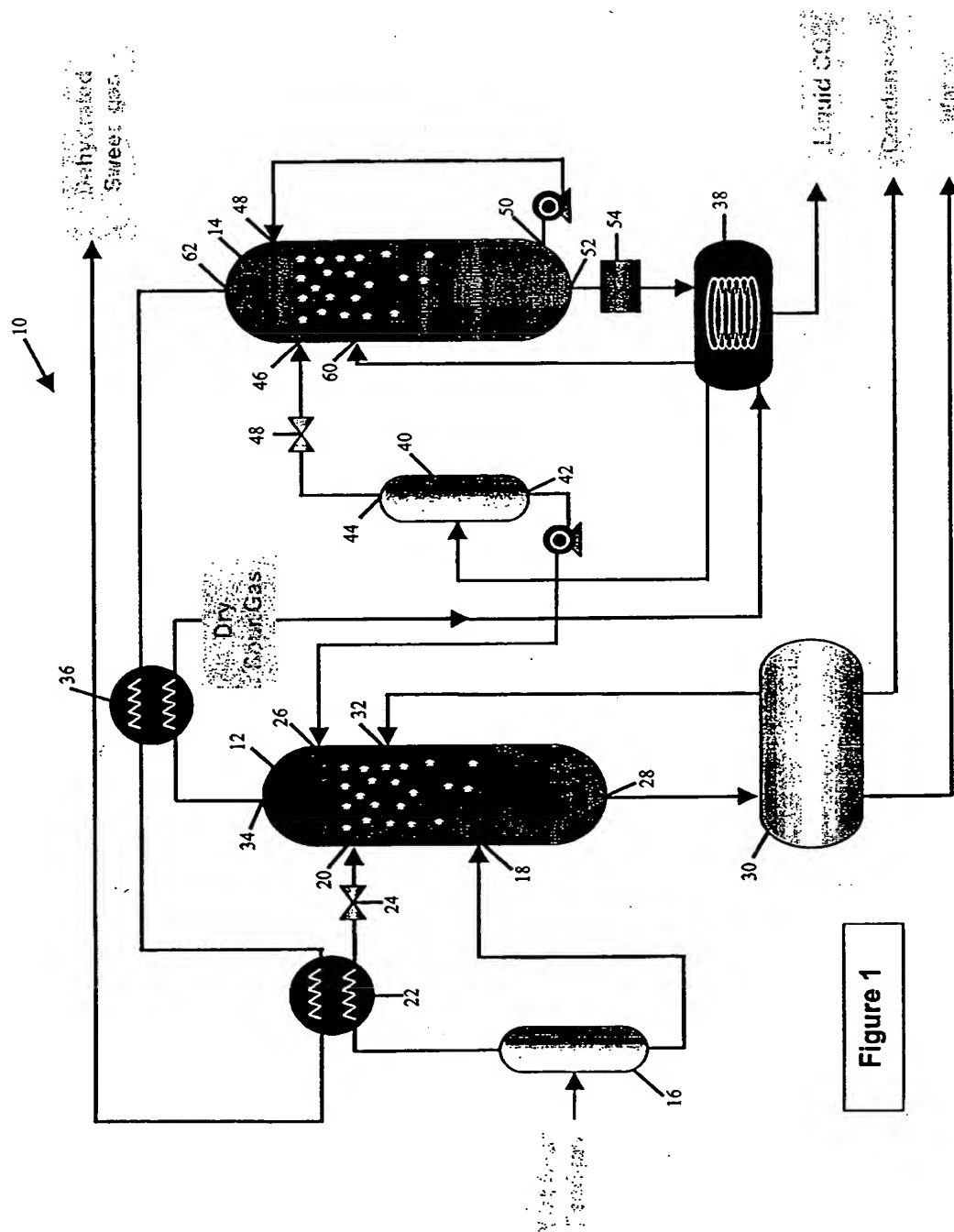


Figure 1

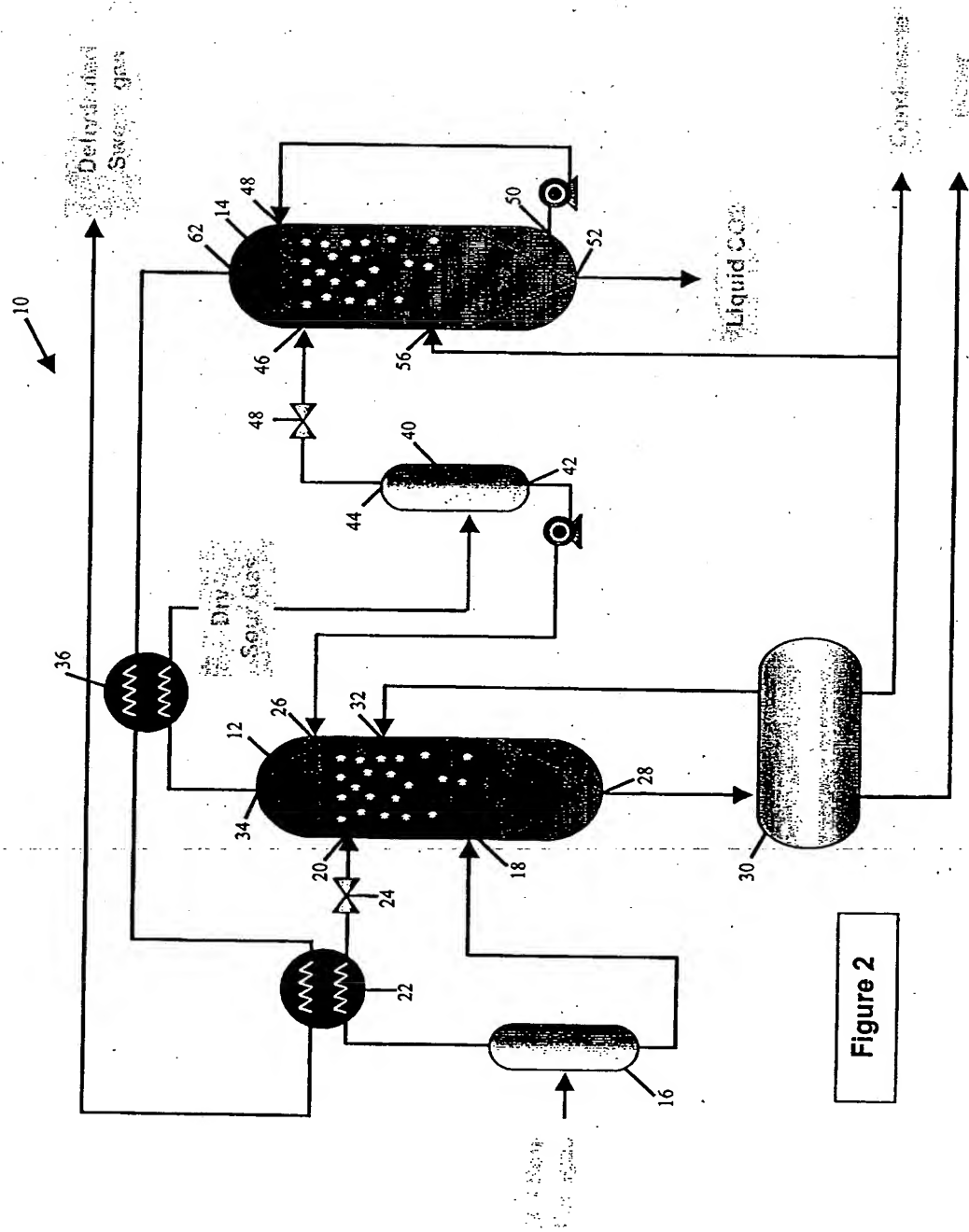


Figure 2

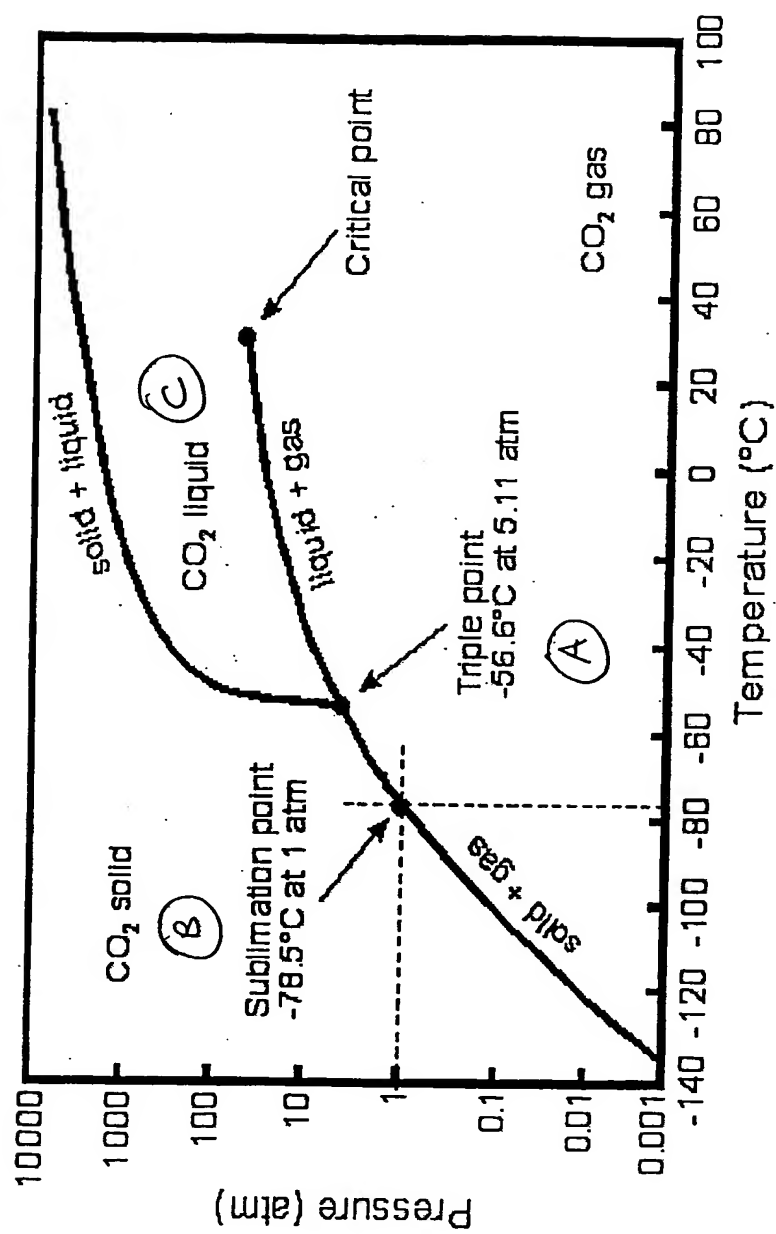


Figure 3

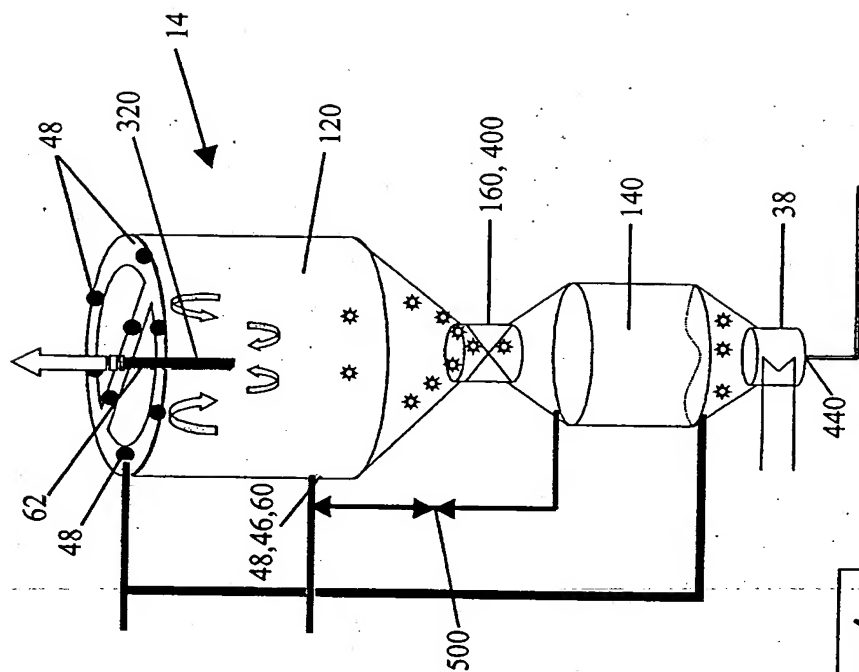


Figure 4

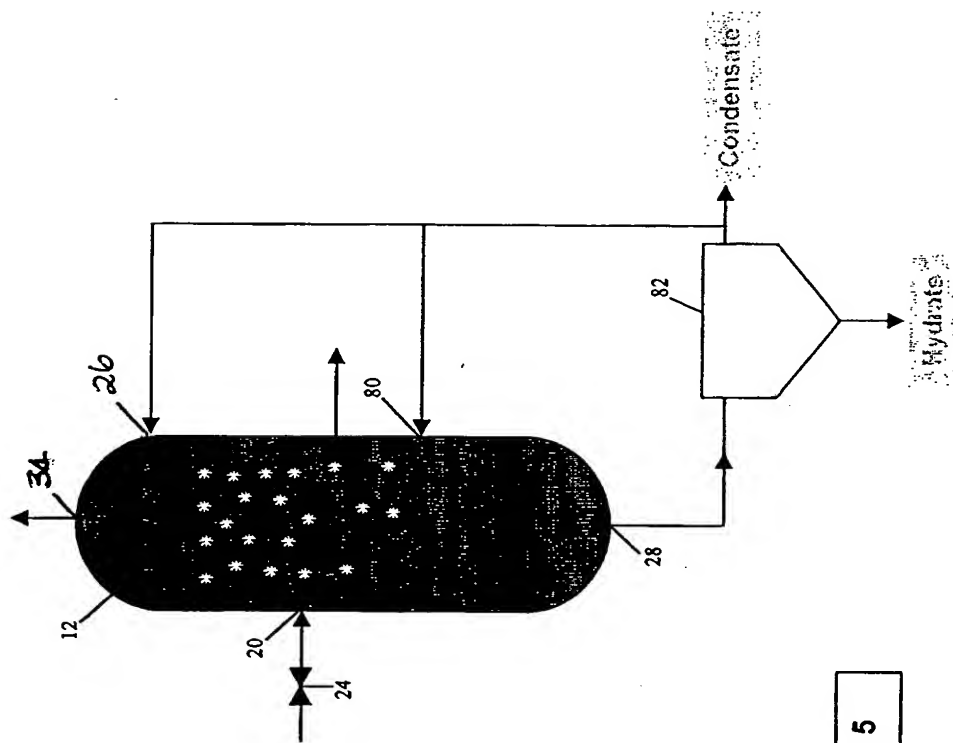


Figure 5

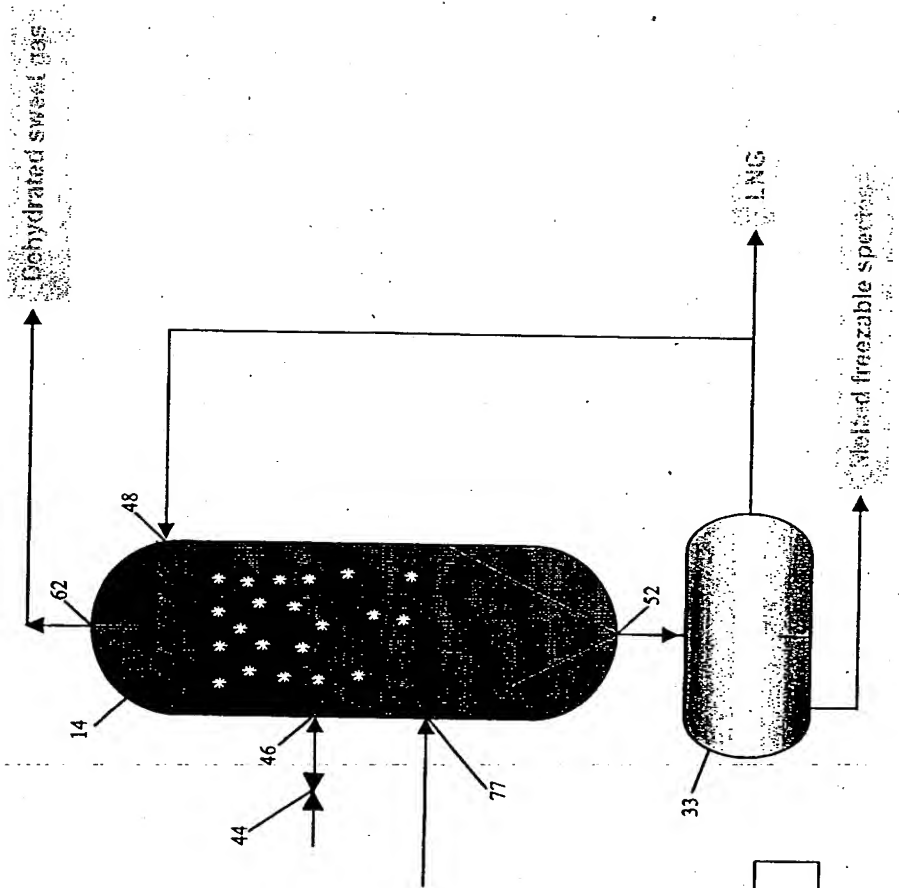


Figure 6

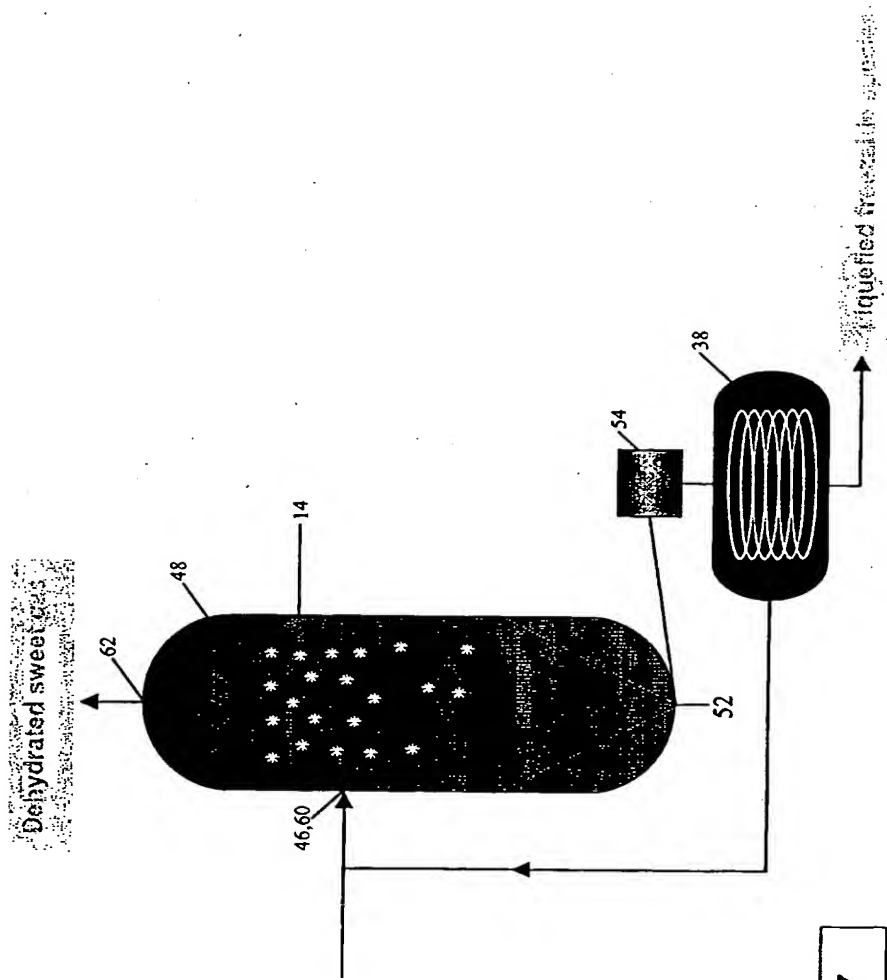


Figure 7

